

STANDARD OPERATING PROCEDURE
METAL SPECIATION

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Title: METAL SPECIATION AND QUANTIFICATION OF PERLITE

APPROVALS:

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Date: _____

SYNOPSIS: A standardized method for speciating metals and perlite particles in solid samples is described. Equipment operating conditions, sample preparation and handling, and statistical equations for data analysis and presentation are included.

REVIEWS:

TEAM MEMBER

SIGNATURE/TITLE

DATE

USEPA Region 8

ISSI Consulting Group, Inc.

Technical Standard Operating Procedures
ISSI Consulting Group, Inc.
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Metal Speciation and Quantification of Perlite

1.0 OBJECTIVES

The objectives of this Standard Operating Procedure (SOP) are to specify the proper methodologies and protocols to be used during metal speciation of various solid samples (including tailings, slags, sediments, dross, bag house dusts, and paint), residential soils and dusts for metals. The metal speciation data generated from this SOP may be used to assess the solid samples as each phase relates to risk. Parameters to be characterized during the speciation analyses include particle size, associations, stoichiometry, frequency of occurrence of metal-bearing forms and relative mass of metal-bearing forms. In addition, aliquots of solid samples can be analyzed separately for perlite, using the same methodology. Perlite particles are counted and sized based on the mineral constituents of each particle. This electron microprobe (EMP) technique, instrument operation protocols and sample preparation to be used during implementation of the Metals Speciation SOP are discussed in the following sections.

2.0 BACKGROUND

To date, numerous metal-bearing forms of soils have been identified from various environments within western mining districts (Table 2-1) (Emmons et al., 1927; Drexler, 1991 per. comm.; Drexler, 1992; Davis et al., 1993; Ruby et al., 1994; CDM, 1994; WESTON, 1995). This listing does not preclude the identification of other metal-bearing forms, but only serves as an initial point of reference. Many of these forms are minerals with varying metal concentrations (e.g., lead phosphate, iron-lead oxide, and slag). Since limited thermodynamic information is available for many of these phases and equilibrium conditions are rarely found in soil environments, the identity of the mineral class (e.g., lead phosphate) will be sufficient and exact stoichiometry is not necessary.

It may be important to know the particle-size distribution of metal-bearing forms in order to assess potential risk. It is believed that particles less than 250 microns (μm) are most available for human ingestion and/or inhalation (Bornschein, et al., 1987). For this study, the largest dimension of any one metal-bearing form will be measured and the frequency of occurrence weighted by that dimension. Although not routinely performed, particle area can be determined. It has been shown (CDM, 1994) that data collected on particle area produces similar results. These measurements add a considerable amount of time to the procedure and limit the total number of particles or samples that can be observed in a study.

Mineral association may have profound effects on the ability for solubilization. For example, if a lead-bearing form in one sample is predominantly found within quartz grains while in another sample it is free in the sample matrix, the two samples are likely

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to pose significantly different risk levels to human health. Therefore, associations of concern include the following:

- 1) free or liberated
- 2) inclusions within a second phase
- 3) cementing
- 4) alteration rims

3.0 SAMPLE SELECTION

Samples should be selected and handled according to the procedure described in the Project Plan.

4.0 SCHEDULE

A schedule for completion of projects performed under this Metals Speciation SOP will be provided in writing or verbally to the contractor along with monthly reporting requirements if large projects are performed. These schedules are based on an aggressive analytical program designed to ensure that the metals speciation analyses are completed in a timely period. Monthly reports are expected to reflect schedule status.

5.0 INSTRUMENTATION

Speciation analyses will be conducted at the Laboratory for Environmental and Geological Studies (LEGS) at the University of Colorado, Boulder or other comparable facilities. Primary equipment used for this work will include:

Electron Microprobe (JEOL 8600) equipped with four wavelength spectrometers, energy dispersive spectrometer (EDS), BEI detector and the TN-5600 data processing system. RJ Lee ZEPPELIN and DATALINK hardware may be used for image storage and processing. An LEDC spectrometer crystal for carbon and LDE-1 crystal for oxygen analyses will be used.

6.0 PRECISION AND ACCURACY

The precision of the EMP speciation will be evaluated based on sample duplicates analyzed at a frequency of 10%. The accuracy of the analyses will be estimated based on a number of methods, depending on the source of the data. Data generated by the "EMP point count" will be evaluated statistically based on the methods of Mosimann (1965) at

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the 95% confidence level on the frequency data following Equation 1.

$$E_{0.95} = 2P(100-P)/N \quad (\text{Eq. 1})$$

Where: $E_{0.95}$ = Probable error at the 95% confidence level
 P = Percentage of N of an individual metal-bearing phase based on percent length frequency
 N = Total number of metal-bearing grains counted

For arsenic, the goal is to count 200 particles and the goal for lead is to count 100 particles. In the event that these goals are achieved in less than 8 hours, particle counting of Pb and As will be discontinued but counts of the other target metals (Cd, Zn, In, Tl, Se, Hg and Sb) will continue until the 8 hours has expired. NIST 2710 or 2711 "Montana soils" will be speciated for traceability.

Quantitative elemental analysis, primarily performed on slag or other variable, metal-bearing forms, will have precision and accuracy evaluated on counting statistics and reproducibility of NIST or other certified standards using conventional EMP methods. In general, site-specific concentrations for these variable, metal-bearing forms will be determined by performing "peak counts" on the appropriate wavelength spectrometer. Average concentrations will then be used for further calculations. Data on specific gravity will be collected from referenced databases or estimated based on similar compounds.

7.0 PERSONNEL RESPONSIBILITY

The analysts will carefully read this SOP prior to any sample examination.

It is the responsibility of the laboratory supervisor and designates to ensure that these procedures are followed, to examine quality assurance (QA) and replicate standards, and to check EDS and WDS calibrations. The laboratory supervisor will collect results, ensure they are in proper format, and deliver them to the contractor.

Monthly reports summarizing all progress, with a list of samples speciated to date with data analyses sheets (DAS), will be submitted each month.

It is also the responsibility of the laboratory supervisor to notify the contractor representative of any problems encountered in the sample analysis process.

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8.0 METHODOLOGY

8.1 Sample Preparation

Grain mounts, 1.5 inches in diameter, of each sample will be prepared using air-cured epoxy. The grain mounting is performed as follows:

- 1) Log the samples for which polished mounts will be prepared.
- 2) Inspect all disposable plastic cups, making sure each is clean and dry.
- 3) Label each "mold" with its corresponding sample number.
- 4) All samples will be split to produce a homogeneous 1-4 gram sample.

NOTE: Separate splits for perlite must be prepared.

- 5) Mix epoxy resin and hardener according to manufacturer's directions.
- 6) Pour 1 gram of sample into mold. Double check to make sure sample numbers on mold and the original sample container match. Pour epoxy into mold to just cover sample grains.
- 7) Use a new wood stirring stick with each sample, carefully blend epoxy and grains so as to coat all grains with epoxy.
- 8) Set molds to cure at ROOM TEMPERATURE in a clean restricted area. Add labels with sample numbers and cover with more epoxy resin. Leave to cure completely at room temperature.
- 9) One at a time remove each sample from its mold and grind flat the back side of the mount.
- 10) Use 600 grit wet abrasive paper stretched across a grinding wheel to remove the bottom layer and expose as many mineral grains as possible. Follow with 1000 grit paper.

NOTE: perlite samples should be mounted on glass thin sections prior to polishing. Perlite particle counts should be counted under polarized transmitted light.

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- 11) Polish with 15 μm oil-based diamond paste on a polishing paper fixed to a lap. Use of paper instead of cloth minimizes relief.
- 12) Next use 6 μm diamond polish on a similar lap.
- 13) Finally polish the sample with 1 μm oil-based diamond paste on polishing paper, followed by 0.05 μm alumina in water suspension. The quality should be checked after each step. Typical polishing times are 30 minutes for 15 μm , 20 minutes for 6 μm , 15 minutes for 1 μm , and 10 minutes for 0.05 μm .

NOTE: use low speed on the polishing laps to avoid "plucking" of sample grains.

- 14) Samples should be completely cleaned in an ultrasonic cleaner with isopropyl alcohol or similar solvent to remove oil and fingerprints.
- 15) To ensure that no particles of any metal are being cross-contaminated during sample preparation procedures, a blank (epoxy only) mold will be made every 20th sample (5% of samples) following all of the above procedures. This mold will then be speciated along with the other samples.
- 16) Each sample must be carbon coated. Once coated, the samples should be stored in a clean, dry environment with the carbon surface protected from scratches or handling.

8.2 Point Counting

Counts are made by traversing each sample from left-to-right and top-to-bottom as illustrated in Figure 8-2. The amount of vertical movement for each traverse would depend on magnification and CRT (cathode-ray tube) size. This movement should be minimized so that NO portion of the sample is missed when the end of a traverse is reached. Two magnification settings generally are used. One ranging from 40-100X and a second from 300-600X. The last setting will allow one to find the smallest identifiable (1-2 micron) phases.

The portion of the sample examined in the second pass, under the higher magnification, will depend on the time available, the number of metal-bearing particles, and the complexity of metal mineralogy. A maximum of 8 hours will be spent per sample.

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8.3 Data Presentation

Analysts will record data as they are acquired from each sample using the LEGS software, which places all data in a spreadsheet file format. Columns have been established for numbering the metal-bearing phase particles, their identity, size of longest dimension in microns, along with their association (L = liberated, C = cementing, R = rimming, I = included) (Figure 8-3). The analyst may also summarize his/her observations in the formatted data summary files.

The frequency of occurrence and relative metal mass of each metal-bearing form as it is distributed in each sample will be depicted graphically as a frequency bar-graph. The particle size distribution of metal-bearing forms will be depicted in a histogram. Size-histograms of each metal-bearing form can be constructed from data in the file.

Data from EMP will be summarized using two methods. The first method is the determination of FREQUENCY OF OCCURRENCE. This is calculated by summing the longest dimension of all the metal-bearing phases observed and then dividing each phase by the total.

Equation 2 will serve as an example of the calculation.

$$F_M \text{ in phase-1} = \frac{\sum (PLD)_{\text{phase 1}}}{\sum (PLD)_{\text{phase-1}} + \sum (PLD)_{\text{phase-2}} + \sum (PLD)_{\text{phase-n}}} \quad (\text{Eq. 2})$$

Where:

F_M = Frequency of occurrence of metal in a single phase.

PLD = An individual particle's longest dimension

$\%F_M \text{ in phase-1} = F_M \text{ in phase-1} * 100$

These data thus illustrate which metal-bearing phase(s) are the most commonly observed in the sample or relative volume percent.

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The second calculation used in this report is the determination of RELATIVE METAL MASS. These data are calculated by substituting the PLD term in the equation above with the value of M_M . This term is calculated as defined below.

$$M_M = FM * SG * ppm_M \quad (\text{Eq. 3})$$

Where:

$$\begin{aligned} M_M &= \text{Mass of metal in a phase} \\ SG &= \text{Specific Gravity of a phase} \\ ppm_M &= \text{Concentration in ppm of metal in a phase} \end{aligned}$$

The advantage in reviewing the RELATIVE METAL MASS determination is that it gives one information as to which metal-bearing phase(s) in a sample are likely to control the total bulk concentration for a metal of interest. For example, PHASE-1 may comprise 98% relative volume of the sample; however, it has a low specific gravity and contains only 1,000 parts per million (ppm) arsenic. PHASE-2 comprised 2% of the sample, has a high specific gravity, and contains 850,000 ppm of arsenic. In this example it is PHASE-2 that is the dominant source of arsenic to the sample.

Finally, a concentration for each phase is calculated. This quantifies the concentration of each metal-bearing phase. This term is calculated as defined below (Eq. 4).

$$ppm_M = M_M * \text{Bulk metal concentration in ppm} \quad (\text{Eq. 4})$$

8.4 Analytical Procedure

A brief visual examination of each sample will be made, prior to EMP examination. This examination may help the operator by noting the occurrence of slag and/or organic matter. Standard operating conditions for quantitative and qualitative analyses of metal-bearing forms are given in Table 8-1. Quality control will be maintained by analyzing standards and duplicates at regular intervals (Section 8.5).

The backscattered electron images will be examined using two settings: one for light-element matrices (slag or organic) and the second for heavy-element matrices (lead sulfide or lead carbonate etc.). This procedure will minimize the possibility that metal-bearing minerals may be overlooked during the scanning of the polished grain mount. The scanning will be done manually in a manner similar to that depicted in Figure 8-2. Typically, the magnification used for scanning all samples except for airborne samples will be 40-100X and 300-600X. The last setting will allow the smallest identifiable (1-2 μm) phases to be found. Once a candidate particle is identified, then the backscatter image will be optimized to discriminate any different phases that may be making up the

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particle or defining its association. Identification of the metal-bearing phases will be done using both EDS and WDS on a EMP, with spectrometers peaked at sulfur, oxygen, carbon and the metal of concern (M). The size of each metal-bearing phase will be determined by measuring in microns the longest dimension.

As stated previously, a maximum of 8 hours will be spent in scanning and analyzing each mount. For arsenic, the goal is to count 200 particles and the goal for lead is to count 100 particles. In the event that these goals are achieved in less than 8 hours, particle counting of Pb and As will be discontinued but counts of the other target metals (Cd, Zn, In, Tl, Se, Hg and Sb) will continue until the 8 hours has expired. NIST 2710 or 2711 "Montana soils" will be speciated for traceability.

Perlite distribution will be examined under polarized transmitted light, and will be counted according to particle size and chemical constituents. Perlite particles will be sorted according to the presence of the following minerals:

- Si
- Si-Al
- Si-Al-Fe
- Si-Al-Ca-Fe

Quantitative Analyses

Quantitative analyses are required to establish the average metal content of the metal-bearing minerals, which have variable metal contents as: Iron-(M) sulfate, Iron-(M) oxide, Manganese-(M) oxide, organic, and slag. These determinations are important, especially in the case of slag, which is expected to have considerable variation in their dissolved metal content. Results will be analyzed statistically to establish mean values. They may also be depicted as histograms to show the range of metal concentrations measured as well as the presence of one or more populations in terms of metal content. In the later case, non-parametric statistics may have to be used or the median value has to be established.

Associations

The association of the metal-bearing forms will be established from the backscattered electron images. Particular attention will be paid in establishing whether the grains are totally enclosed, encapsulated or liberated. The rinds of metal-bearing grains will be identified. Representative photomicrographs of backscatter electron images establishing the association of the principal metal-bearing forms will be obtained for illustration purposes. A positive/negative, black and white film (Polaroid 55) will be used or a 128x128 (minimum) binary image in ".tif" format may be stored. Recorded on each

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photomicrograph and negative will be a scale bar, magnification, sample identification and phase identification. Abbreviations for the identified phases should be used. Examples are listed in Table 8-2. A final list must be submitted with the laboratory report.

8.5 Instrument Calibration and Standardization

The WDS will have spectrometers calibrated for the metal of concern, carbon, oxygen and sulfur on the appropriate crystals using mineral standards. The EDS will have multi-channel analyzer (MCA) calibrated for known peak energy centroids. Calibration will be performed so as to have both low (1.0-3.0 KeV) and high (6.0-9.0 KeV) energy peaks fall within 0.05 KeV of its known centroid.

The magnification marker on the instrument will be checked once a week. This will be performed by following manufacturer instructions or by measurement of commercially available grids or licite spheres. Size measurements must be within 4 microns of certified values.

Initial calibration verification standards (ICVs) must be analyzed at the beginning of each analytical batch or once every 24 hours, whichever is more frequent. A set of mineral or glass standards will be run quantitatively for the metal of concern, sulfur, oxygen and carbon. If elemental quantities of the ICVs do not fall within +/- 5% of certified values for each element, the instrument must be recalibrated prior to analysis of investigative samples.

The metal-bearing forms in these samples will be identified using a combination of EDS, WDS and BEI. Once a particle is isolated with the backscatter detector, a 5-second EDS spectra is collected and peaks identified. The count rates for the metal(s) of concern, sulfur, carbon and oxygen can be either visually observed on the wavelength spectrometers or K-ratios calculated.

9.0 PERSONAL HEALTH AND SAFETY

Each individual operating the KEVEX x-ray fluorescence or electron microprobe instruments will have read the "Radiation Safety Handbook" prepared by the University and follow all State guidelines for operation of X-ray equipment.

Latex gloves and particulate masks will be worn during preparation of sample cups. All material that comes in contact with the samples or used to clean work surface areas will be placed in poly-bags for disposal.

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10.0 FINAL REPORT

A final laboratory report will be provided to the Contractor. The report will include all EMP data including summary tables and figures. Individual sample data will be provided on disk.

Speciation results will include: 1) a series of tables summarizing frequency of occurrence for each metal phase identified along with a confidence limit; 2) summary histograms of metal phases identified for each waste type; 3) a summary histogram of particle size distribution in each waste type; and 4) a summary of metal phase associations. Representative photomicrographs or TIFF images will also be included in the final report.

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11.0 REFERENCES

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Table 2-1

Metal-Bearing Forms Found Within Western Mining and Smelting Districts

OXIDES

Lead Oxide
Manganese (metal) oxide
Iron (metal) oxide
Lead molybdenum oxide
Arsenic Oxide
Cadmium Oxide
Copper Oxides
Zinc Oxide
Lead Arsenate
Arsenic Trioxide
Calcium (metal) oxide

SILICATES

Slag
Lead silicate
Arsenic silicate
Zinc silicate
Clays

SULFATES

Iron (metal) sulfate
Lead sulfate
Lead barite
Zinc Sulfate
Arsenic sulfate
Copper sulfate

CARBONATES

Lead Carbonate
Zinc Carbonate

PHOSPHATES

(metal) phosphates

SULFIDES

Lead sulfide
Sulfur-containing salts
Iron-arsenic sulfide
Zinc sulfide
Copper sulfides
Copper-iron sulfide
Cadmium Sulfide

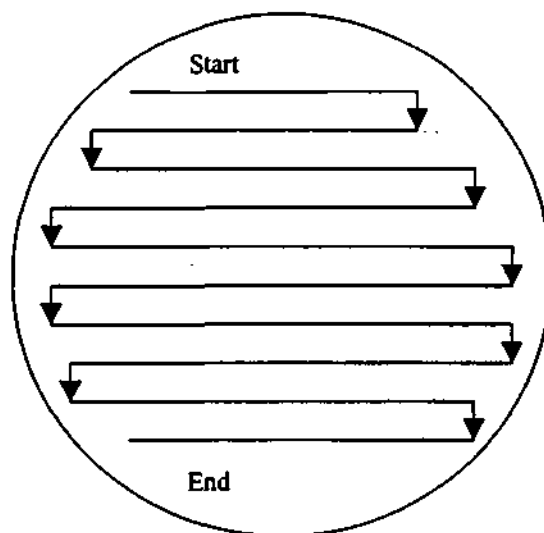
OTHER

Native: Lead, Copper,
Cadmium, Mercury, Indium,
Thallium, Selenium

Lead/Arsenic/Cadmium/Mercury
Chlorides
Lead paint
Solder
Organic lead
Lead vanadate
Minor telluride, and bismuth-lead
phases

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Figure 8-2



ASSAY _____
SAMPLE ID _____
ANALYST _____
TIME START _____

Pb ASSAY _____
LAB _____
TIME END _____

Figure 8-3

[illegible]

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Table 8-1

EMP Standard Operating Conditions

	WDS	EDS
Accelerating Voltage	15 KV	15-20 KV
Beam Size	1-2 microns	1-2 microns
Cup Current	10-30 NanoAmps	10-30 NanoAmps
Ev/Channel	NA	10 or 20
Stage Tilt	NA	Fixed
Working Distance	NA	Fixed
MCA time Constant	NA	7.5-12 microseconds
X-ray lines	S K-alpha PET O K-alpha LDE1 C K-alpha LDEC Zn K-alpha PET As L-alpha TAP Cu K-alpha LIF Cd L-alpha PET Pb M-alpha PET Pb L-alpha LIF In L-alpha PET Tl L-alpha LIF Hg L-alpha LIF Se L-alpha LIF Sb L-alpha PET	S K-alpha 2.31 KeV O K-alpha 0.52 KeV C K-alpha 0.28 KeV Pb M-alpha 2.34 KeV Pb L-alpha 10.5 KeV Zn K-alpha 8.63 KeV Cu K-alpha 8.04 KeV As K-alpha 10.5 KeV As L-alpha 1.28 KeV Cd L-alpha 3.13 KeV In L-alpha 3.28 KeV Tl M-alpha 2.27 KeV Tl L-alpha 10.26 KeV Hg L-alpha 9.98 KeV Hg M-alpha 2.19 KeV Se L-alpha 1.37 KeV Sb L-alpha 3.60 KeV

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Table 8-2

Suggested Abbreviation for Photomicrographs

Metal-bearing Phase	Abbreviation
In	In
Tl	Tl
Hg	Hg
Se	Se
Sb	Sb
Lead Sulfide	Ga
Lead Sulfate	Ang
Lead Carbonate	Cer
Mn-(M) Oxide	Mn(M)
Fe-(M) Oxide	Fe(M)
(M)Phosphate	(M)Phos
Fe-(M) Sulfate	Fe(M)Sul
Metal Oxide	(M)O
Pb-Mo Oxide	Wulf
Slag	Slag
Metallic Phase	(M)
Metal Silicate	(M)Si
Solder	Sold
Paint	Pnt
Metal-bearing Organic	(M)(Org)
(M) barite	(M)Bar
Pb arsenate	PbAsO
Pb vanadate	PbVan
As-Sb Oxide	AsSbO
Chalcopyrite	Cp
Sphalerite	Sph
Arsenopyrite	Apy